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Functional Nanostructured Materials (including low-D carbon)

Carbon Dots exhibiting Concentration-Dependent Full-Visible-Spectrum Emission for Light-Emitting Diode Applications

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Carbon Dots exhibiting Concentration-Dependent Full-Visible-Spectrum Emission for Light-Emitting Diode Applications

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ABSTRACT: Carbon dots (CDs) that exhibit emission over the whole visible spectrum are desired for using in light-emitting diodes. Here, CDs displaying tunable fluorescence over the whole visible region are synthesized. Different concentrations of CDs are uniformly dispersed in epoxy resin and coated on 405-nm LED chips to obtain monochrome blue, cyan, green, yellow, red, and deep red LEDs that yield a color gamut covering 99.4% of the National Television Standards Committee (NTSC) standard. These monochrome LEDs display similar stability decay curves. Furthermore, warm and neutral white LEDs are produced by coating cyan- and red-emitting CD layers on 405-nm LED chips, achieving color rendering indexes (CRI) of 96.4 and 96.6, respectively. Two fluorescent conversion layers derived from one material at different concentrations simplifies the preparation of high-CRI white LEDs. The uniform weak changes of the cyan and red PL peaks during operation ensures the high stability of these CD-based white LEDs. This research provides a new avenue to develop low-cost, easy-to-prepare CDs with tunable emission colors as alternative phosphors for LED-based high-performance displays and lighting.

KEYWORDS: concentration-dependent spectrum-tunable carbon dots, full-visiblespectrum emission, monochrome light-emitting diodes, high color rendering index, white-light-emitting diodes

INTRODUCTION

Nowadays, light-emitting diodes (LEDs) have drawn much attention for use in lighting and displays because of their small volume, light weight, low-power consumption, and durability.¹⁻³ White light-emitting diodes (WLEDs) should emit warm light with a color rendering index (CRI) over 90 and a correlated color temperature (CCT) below 4000K to ensure health, increase the secretion of melatonin, and avoid eye fatigue.⁴⁻⁶ Current warm WLEDs are composed of an ultraviolet (UV)/blue pump LED and color convertors, often called phosphors, which play an important role in WLED performance, such as production cost, Commission Internationale d'Éclairage (CIE) coordinates, CRI, CCT, and luminous efficiency. However, commonly used rare earth phosphors are expensive and have limited resources.⁷ Conventional quantum dots (QDs) and common perovskite QDs are potentially toxic because they contain heavy metals such as indium, cadmium or lead.⁸⁻¹⁰ Consequently, low-cost, non-toxic alternative luminescent materials are indispensable for the improvement of WLEDs.

Recently, carbon dots (CDs) have emerged as promising phosphors for the development of WLEDs and displays because they possess attractive characteristics including low cost, easy preparation, excellent luminescent properties, high chemical stability, and low toxicity.¹¹⁻¹⁷ In particular, CDs with the characteristic multiple emission centers makes them ideal candidates for LED displays and high-CRI warm WLEDs.^{18,19}

Wang et al. developed a UV-pumped warm WLED (CRI = 97) by combining blue-, green-, and red-emitting CDs.²⁰ Miao et al. reported blue-, green-, and red-emitting CDs

that were used to fabricate warm WLEDs with a CRI of 92.²¹ These reports highlighted the potential applications of CDs in WLEDs. However, the use of multiple phosphors increases the preparation cost and their different degradation rates may change the emission spectrum with runtime, and lead to undesirable changes in the photometric performance of WLEDs.²² Moreover, red fluorescent CDs are scarce and require intricate synthesis and purification processes.²³⁻²⁵ A single kind of fluorescent CDs that exhibit multiple emission colors under a same excitation wavelength is desirable to avoid these issues.

In our previous studies of the CDs synthesized by citric acid and hydroxylcontaining amino compounds, we demonstrated that the synergistic effect of graphitic nitrogen (N) and electron-donating hydroxyl groups resulted in an extremely high photoluminescence (PL) quantum yield of nearly 100%.²⁶ We found that the PL of the CDs prepared from a certain molar ratio of precursors in this system could be tuned throughout the full-visible light region by simply changing the CDs concentration, thereby obtaining deep blue, blue, cyan, green, yellow, orange, red, and deep red fluorescence emission without complicated synthesis and purification processes.

Herein, citric acid (CA) is used as the carbon (C) source and various hydroxylcontaining amino compounds are used as nitrogen (N) sources to prepare a series of Ndoped CDs. The concentration-dependent PL behavior of the CDs is systematically evaluated. Simply changing the concentration of CDs in epoxy resin can produce blue, cyan, green, yellow, red, and deep red convertors, which can be separately applied on 405-nm LED chips to fabricate monochrome blue, cyan, green, yellow, red, and deep

red LEDs, respectively. These LEDs yield a color gamut covering 99.4% of the National Television Standards Committee (NTSC), demonstrating that concentration-dependent spectrum-tunable CDs are promising for display applications. Warm and neutral WLEDs with CRI values of 96.4 and 96.6, respectively, are also fabricated that are located on the Planckian locus, indicating high-quality lighting.

MATERIALS AND METHODS

Materials: CA (99.5%), serine (99%), n-propanolamine (99%), isopropanolamine (99%), ethylenediamine (99.5%), and deionized water were purchased from Shanghai Macklin Biochemical. Monoethanolamine (MEA; 99.5%), threonine (99%), ethylenediamine (99%), and tris(hydroxylmethyl)aminomethane (99%) were purchased from Shanghai Aladdin Bio-Chem Technology.

Abbreviations for different CDs: M-CDs is a general term that stands for the CDs synthesized by the reaction of CA and MEA, while M-CD(1:X) represents the CDs synthesized by the precursors in a molar ratio of 1:X, specifically, M-CD equals to M-CD(1:1.5). In this way, "S" in S-CD stands for serine, "I" in I-CD stands for isopropanolamine, "T" in T-CD stands for threonine, "N" in N-CD stands for n-propanolamine, "E" in E-CD stands for ethylenediamine, "Tr" in Tr-CD stands for tris(hydroxylmethyl)aminomethane.

Synthesis of M-CD: CA (3.15 g) and of MEA (1.5 mL) were dissolved in deionized water (15 mL) and then heated in a microwave oven (350 W). The heating process was paused every 30 s to stir the mixture and avoid bumping (the heating curve is shown in

Figure S1). After 5 min, anhydrous ethanol was added and then the mixture was centrifuged at 10000 rpm (6640g) for 10 min to remove precipitated aggregates. The mixture was transferred into a freezing dryer, froze for one hour at -40°C, then stored in vacuum environment of less than 5 pa for 5 hours to obtain dry CDs powder.

Synthesis of Other CDs: S-CD, I-CD, T-CD, N-CD, E-CD, and Tr-CD were synthesized by the corresponding precursors in the manner of synthesis M-CD.

The yields of these as-prepared CDs: The yields can be calculated by the ratio of the weight of the obtained powder to the weight of the raw materials (without water). These results were shown in Table S1.

M-CD/epoxy colloid preparation: Blue fluorescent M-CD aqueous solution (0.3 g, 20 mg mL⁻¹) and epoxy resin (1.5 g) were thoroughly mixed and heated at 50 °C for 30 min. Then the mixture was rapidly stirred until it became a slightly viscous colloid. Other colloids were prepared by corresponding fluorescent M-CD aqueous solution and treated as described for the blue fluorescent colloid.

M-CD/epoxy column preparation: Different fluorescent colloid was separately injected into a cylindrical mold, which was then heated at 50 °C for 12 h (curing condition) to form corresponding fluorescent column.

Monochrome LED fabrication: Blue fluorescent colloid (0.15 g) was added dropwise onto a 405-nm LED chip, cured by heating to give a monochrome blue LED. Other monochrome LEDs were fabricated using the corresponding fluorescent colloids.

WLED fabrication.

Warm WLED: Red fluorescent colloid (0.010 g) was dropped onto a 405-nm LED

 chip. After curing, cyan fluorescent colloid (0.018 g) was added as a second layer and then cured to give a warm WLED.

Neutral WLED: Cyan fluorescent colloid (0.035 g) was dropped onto a 405-nm LED chip. After curing, red fluorescent colloid (0.013 g) was dropped as the second layer and then cured to give a neutral WLED.





Figure 1. (a) Fluorescence of M-CD solutions with concentrations of 0.1, 1, 5, 10, 20, 50, and 100 mg mL⁻¹ excited at their optimal excitation wavelengths, (b) corresponding normalized PL spectra, and (c) CIE color coordinates in color gamut. Bluest, greenest,

and reddest excitation–emission matrices of (d) 0.1, (e) 10, and (f) 100 mg mL⁻¹ M-CD solutions, respectively. The color bar is the normalized fluorescence intensity. Normalized PL spectra of (g) S-CD, (h) I-CD, and (i) T-CD solutions of various concentrations.

First, the PL properties of the four types of CDs were investigated. Figure 1a shows the fluorescence of M-CD solutions with different concentrations of 0.1, 1, 5, 10, 20, 50, and 100 mg mL⁻¹, which exhibited emission colors of deep blue, blue, cyan, green, orange, red, and deep red, respectively. Their corresponding normalized PL spectra are displayed in Figure 1b. The emission peak was tuned from 435 to 678 nm as the M-CD concentration increased from 0.1 to 100 mg mL⁻¹, spanning a range of 243 nm, signifying that the M-CD exhibited concentration-dependent tunable PL throughout the full visible region. Figure 1c shows the CIE coordinates of the PL spectra of M-CD solutions at different concentrations. The CIE coordinates covered 82.3% of the NTSC standard, demonstrating that the M-CD have potential for use in variable-color displays and lighting by simply changing the M-CD concentration. For M-CD solutions with concentrations of 0.1, 10, and 100 mg mL⁻¹, their main emission peaks are located at 435, 525, and 678 nm, respectively (Figure 1d) and the corresponding color coordinates are (0.15, 0.1), (0.32, 0.54), and (0.71, 0.29), respectively, denoting the bluest, greenest, and reddest PL, respectively, displayed by the M-CD. In addition, PL spectra of different concentrations of S-CD, I-CD, and T-CD solutions were also explored. As their concentration was increased from 0.1 to 100

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mg mL⁻¹, the PL emission peak of S-CD shifted from 464 to 684 nm (range of 220 nm), the PL emission peak of I-CD shifted from 411 to 602 nm (range of 191 nm), and that of T-CD shifted from 420 to 554 nm (range of 134 nm) (Figure 1g–i).

We also studied the PL of CDs synthesized using other molar ratios of the relevant precursors. Figure S2 shows 3D PL spectra of M-CDs, S-CDs, I-CDs, and T-CDs synthesized with a C/N source molar ratio of 1:0.5. Figure S3 depicts the 3D PL spectra of S-CD, I-CD, and T-CD, and Figure S4 shows the 3D PL spectra of the four types of CDs fabricated with a C/N ratio of 1:3. The PL spectra revealed that the PL peaks of these N-doped CDs red-shifted markedly as the CD concentration increased, meaning that they all displayed concentration-dependent PL behavior. However, the magnitudes of the spectral shifts were different. As shown in Figure S5, when the C/N ratio of the precursors was 1:1.5, the spectral shifts of the obtained CDs (that is, M-CD, S-CD, I-CD, and T-CD) were the largest compared with those for the CDs produced using other C/N ratios.

N-Propanolamine, ethylenediamine, and tris(hydroxylmethyl)aminomethane were also chosen as N sources to synthesize CDs using a C/N molar ratio of 1:1.5. When the CDs concentration was increased from 0.1 to 100 mg mL⁻¹, the spectral shifts of the CDs were 196, 146, and 126 nm (Figure S6–S8). The chemical formulas of these N sources are compared in Figure S9. Serine, isopropanolamine, and threonine all have ethanolamine-like structures and differ by the presence of a carboxyl group, methyl group, and carboxyl and methyl groups, respectively. Both carboxyl and methyl groups have inhibitory effects on concentration-dependent tunable PL, and the effect of methyl groups is stronger than that of carboxyl groups. Moreover, comparing the molecular formulas of MEA, n-propanolamine, ethylenediamine, and tris(hydroxylmethyl)aminomethane indicated that long carbon chains, excess amino groups, and hydroxyl groups in the N source all narrowed the range of spectral tuning caused by concentration modulation.



Figure 2. (a) TEM image of M-CD. Top inset: size distribution histogram; bottom inset: high-resolution TEM image. (b) FTIR spectra of M-CD, S-CD, I-CD and T-CD. XPS analysis of M-CD, S-CD, I-CD and T-CD: (c) survey scan and (d) C 1s, (e) N 1s, and (f) O 1s spectra.

The concentration-dependent PL properties of these CDs were probed by morphologies and chemical compositional characterizations. A transmission electron microscopy (TEM) image of M-CD is shown in **Figure 2**a, which revealed that the M-CD particles were torispherical in dilute solution. The top inset of Figure 2a illustrates a Gaussian size distribution of M-CD with a full width at half maximum (FWHM) of 0.8 nm, indicating that the particle size was relatively uniform. A high-resolution TEM image of the M-CD (bottom inset of Figure 2a) revealed an in-plane lattice spacing of 2.1 Å in graphite (100 facet).²⁷ The size distribution of M-CD with the concentration of 20 mg mL⁻¹ can be fitted by two Gaussian distributions with mean values of 2.6 and 7.0 nm, respectively. The former data was consistent with that of the monodispersed M-CD in dilute solution (Figure S10b). The HRTEM in Figure S10b demonstrated that the large CDs are agglomerated with small ones. These results indicate that aggregation of CDs begins to occur as concentration increases. Figure S10c show that M-CD are greatly agglomerated in solution with concentration of 100 mg mL⁻¹. The aggregation degree of M-CD is increasing while elevating the concentration. The aggregation degree are corresponded to emission wavelengths: lower aggregation degree are corresponded to shorter emission wavelength, and longer emission wavelength are in response to higher aggregation degree. That is similar to the size-dependent PL properties, which state that increasing the particle size will cause a red-shift in emission wavelength because of the quantum confinement effect.²⁸⁻³⁰

The chemical bonds in the CDs were determined by Fourier transform infrared (FT-IR) spectroscopic analysis (Figure 2b). The observed stretching vibrations of NH (3190 cm⁻¹) and C-N (1063 cm⁻¹) and in-plane bending vibration of N-H (1557 cm⁻¹) verified the N doping of the CDs.^{26,31,32} The observed stretching vibrations of OH (3418 cm⁻¹), C=O (1710 cm⁻¹), carboxylate C=O (1657 and 1400 cm⁻¹), and C-O-C (1251 and 1177 cm⁻¹) and the in-plane bending vibration of O-H (1333 cm⁻¹) indicated that

the CDs were doped with oxygen (O).^{33,32}

The composition of these CDs were further confirmed by X-ray photoelectron spectroscopy (XPS). The three peaks detected in the survey scans indicated that the four types of CDs were composed of C. N. and O elements (Figure 2c). The high-resolution of C 1s spectra showed the presence of sp² C of C=C groups, and sp³ C of C-N/C-O and C=O groups, which were located at 284.6, 286.2, and 288.3 eV, respectively (Figure 2d).^{34,35} Two types of N doping were revealed in the CDs by the high-resolution N 1s spectra (Figure 2e): pyrrolic N and graphitic N, which were located around 399.5 and 400.5 eV.^{36,37} Two peaks existed at 531.7 and 533 eV in the O 1s spectra were corresponding to C=O and C-OH/C-O-C groups, respectively (Figure 2f).^{34,35} XPS analysis of the CDs synthesized using other molar ratios of the precursors was also conducted. Figure S11a shows the XPS analyses of the four types of CDs produced with C/N ratios of 1:0.5 and Figure S11b shows that of the four types of CDs fabricated using a C/N ratio of 1:3. All these spectra are similar to those in Figure 2d–f, meaning that these CDs all have the same chemical compositions but different contents of various functional groups. According to the XPS data, the contents of chemical bonds were calculated and are presented in Figure S12 and Table S2-S4. The CDs synthesized using a C/N molar ratio of 1:1.5 had the highest graphitic N and C-O-C/C-O-H contents of the CDs. We previously studied the concentration-dependent spectral tunability of CDs and found that for CDs synthesized using the same precursors, the higher the content of C-O-C/C-O-H groups, the larger the tunable spectral range.³⁸ This was further confirmed by these CDs possessing the largest tunable spectral range when the

C/N molar ratio was 1:1.5. For the different types of CDs, the concentration-dependent spectral characteristics are mainly caused by the synergistic effect of the band-gap narrowing induced by increasing the CD concentration and content of C-O-C/C-O-H groups.³⁸



Figure 3. Absorption spectra of (a) M-CD, (b) S-CD, (c) I-CD, and (d) T-CD solutions with different concentrations. Tauc plots of different concentrations of (e) M-CD, (f) S-CD, (g) I-CD, and (h) T-CD solutions. The intersection values of these spectra tangents and the X-axis are the band gaps. (i) Energy-level alignments and PL emission maxima of the four types of CDs. (j) Energy-level diagrams of CDs during concentration increasing.

To clarify the mechanisms behind the synergistic effect described above, absorption spectra of different concentrations of the four types of CDs were measured. As shown

in Figure 3a-d, M-CD, S-CD, I-CD, and T-CD solutions exhibited a strong peak between 300 and 400 nm that arose from n- π^* transitions because of C=O bonds.³⁹ As the CD concentration increased, M-CD and S-CD showed obvious reinforcement in the absorption spectral intensity over the broad range from 400 to 600 nm, while that changed little between 400 and 500 nm for I-CD, and T-CD displayed no discernible increase in absorption intensity in the range of 400-500 nm. The absorption spectra were converted to Tauc plots of $(\alpha hv)^2$ for hv to determine the optical band gaps (E_g) of the CDs, where α is absorption coefficient, h is the Planck constant, and v is light frequency.^{40,41} In the Tauc plots (Figure 3e–h), the intersection values on the x-axes are E_g , which decrease as concentration increases, indicating that E_g narrows with increasing CD concentration. The E_g values of the four types of CDs at different concentrations are listed in Table S5. When their concentration increased from 0.1 to 100 mg mL⁻¹, the PL spectral shifts of M-CD, S-CD, I-CD, and T-CD were 243, 220, 191, and 134 nm, respectively, and their E_g were narrowed by 0.55, 0.46, 0.2, and 0.06 eV, respectively. Changes of E_g values and PL emission peaks of the CDs are plotted in Figure 3i. The effect of increasing concentration on the E_g values of M-CD, S-CD, I-CD, and T-CD weakened in turn. The changes in PL peak positions are closely related to the contents of C-O-C/C-O-H groups with sp²-hybridized carbon, which induce hydroxy- or epoxide-related electronic states within the n- π^* gap that can form excited energy levels.^{38,42,43} The energy-level diagram are depicted in Figure 3j. According to the quantum confinement effect, energy levels splitting and broadening occur in CDs' aggregation process and causes a reduction of the band gap.^{38,44,45} Therefore, as the

concentration increases, on one hand, the *Eg* values decrease rapidly, on the other hand, the excited-state energy levels within the $n-\pi^*$ gap also splits and broadens, which makes some excited energy levels easily get into the broadening lowest unoccupied molecular orbital (LUMO) levels, and promotes red-shift of the PL.³⁸ So theoretically all λ_{em} -dependent CDs have concentration-dependent PL behaviors, which are also confirmed by the experiments in our laboratory, but most CDs undergo severe aggregation-caused quenching (ACQ), in which case concentration-dependent tunable PL are too weak to be observed or appreciated.

The relative amounts of C-O-C/C-O-H groups of the M-CD, S-CD, I-CD, and T-CD were 0.124, 0.16, 0.152, and 0.26, respectively, which are the highest among the respective CDs synthesized by using different C/N molar ratios (collectively refer to as M-CDs, S-CDs, I-CDs, and T-CDs). As a result, the four kinds of CDs displayed the largest spectral shifts. However, no direct proportional relationship was observed between the PL spectral shifts of the four types of CDs and the relative contents of C-O-C/C-O-H groups. This demonstrates that the magnitude of the concentration-dependent PL spectral shift of different kinds of CDs are determined by both the narrowing of E_g and the amounts of C-O-C/C-O-H groups, and the former factor dominates the overall effect.



Figure 4. (a) Photographs of M-CD/epoxy composite columns under ambient light (top) and UV light (bottom). (b) Photographs of monochrome blue, cyan, green, yellow, red, and deep red LEDs produced by coating M-CD/epoxy colloid on 405-nm violet chips. (c) Normalized EL spectra of these monochrome LEDs in (b). (d) CIE color coordinates of the monochrome LEDs and WLEDs. (e) EL spectrum of the warm WLED lamp, inset is the photograph during operation. (f) EL spectrum of the neutral WLED lamp and the photograph during operation (inset). (g) Photographs of color pens under the operating warm (top) and neutral (bottom) WLED lamps.

Considering that the concentration-dependent PL of M-CD can be tuned throughout the full visible region, we mixed M-CD and epoxy resin with a variety of ratios to make composite colloids displaying different fluorescence behavior, which were injected into column molds to form M-CD/epoxy columns. As the concentration of M-CD increases in the columns in **Figure 4**a, their color darkens from light yellow to black and their fluorescence gradually shifts from blue to deep red. These results indicate that any desired fluorescence color can be obtained by simply changing the concentration of M-CD. To illustrate the great potential of the concentration-dependent PL CDs for LED-based display and lighting applications, we fabricated monochrome LED lamps by coating M-CD/epoxy colloids with different emission colors on 405-nm violet LED chips. Photographs of monochrome blue, cyan, green, yellow, red, and deep red LED devices during operation are shown in Figure 4b and their normalized electroluminescence (EL) spectra are provided in Figure 4c. The distinct peaks of these monochrome LEDs are located at 472, 503, 527, 578, 629, and 698 nm, respectively, which are marked in Figure 4d as CIE color coordinates of (0.15, 0.24), (0.25, 0.42), (0.33, 0.51), (0.48, 0.51), (0.59, 0.41), and (0.71, 0.29) respectively. By combining with the 405-nm chip, these LEDs can reach 99.4% of the NTSC standard area. Commercially used LCD monitor (Samsung S22F350FH) and projector (Acer K750) were chosen for comparison. Pure blue, green, and red spectra were measured and shown in Figure S13, their color gamut area accounts for 77.1% and 73.8% of the NTSC, respectively, which demonstrates that M-CD-based monochrome LEDs have excellent potential for use in displays. Recently, Yuan et al. synthesized green and red emissive CDs with PLQY of 75% and 72%, respectively, and their corresponding FWHM were only 31 and 33 nm, respectively. By combining with the 450-nm chip, these CDs showed a notable wide-color gamut of 110% NTSC.⁴⁶ Inspired by this article, our next step is to work on narrowing these concentration-dependent tunable spectra make M-CD more conducive to display.

To investigate the stability of these monochrome LEDs, typical blue, green, and

 deep red LEDs were operated continuously for 10 days. These LEDs still remained at about 94% of the initial emission intensity after 10 days (Figure S14 and S15). The intensity attenuation of the three LEDs was almost the same because the fluorescence originated from the same type of M-CD. In addition, their color coordinates hardly changed during operation (Figure S16).

In view of the concentration-dependent multicolor luminescence and identical outstanding stability of M-CD, cyan and red fluorescent M-CD/epoxy colloids were used as color conversion layers in combination with 405-nm LED chips to create WLEDs with high CRI. Red-emitting M-CD/epoxy colloid was coated on a 405-nm LED chip, cured, and then a cyan-emitting M-CD/epoxy colloid was applied and cured to obtain a warm WLED with a CCT of 3058.7 K, CIE color coordinates of (0.430, 0.405), luminous efficiency of 41.2 lm W⁻¹, and CRI of 96.4 (Figure 4e). Changing the coating order of M-CD fluorescent layers provided a neutral WLED with the CCT, CIE coordinates, luminous efficiency and CRI of 5475.4 K, (0.332, 0.355), 46.8 lm W⁻¹ and 96.6, respectively (Figure 4f). As shown in Figure 4e and f, the cyan layer perfectly replaced the blue and green layers used previously and achieved spectra that covered almost the whole visible range from 400 to 800 nm without a notable blue-green cavity.^{20,21,47} Meanwhile, the cyan and red layers made of a single kind of CD greatly simplified the preparation of a high-CRI WLED produced by coating three layers of different CDs displaying blue, green, and red emission, and proper double-layer structure made these WLED have higher luminous efficiencies due to less energy loss.^{20,21} Comparison of the spectra of the warm and neutral WLEDs revealed that their Page 19 of 29

main difference was the intensity of red emission, which is closely related to the coating order of the red layer. This behavior is related to energy conservation: the closer the conversion layer to the LED chip, the stronger the emission of the layer because of the LED chip is used to directly excite the neighboring conversion layer, whereas the emission of the second layer is weakened as part of the pumping light was absorbed by the previous layer. The color coordinates of the warm and neutral WLEDs were all located on the black-body locus in the CIE 1931 color gamut (Figure 4d), indicating that the two WLED lamps produced high-quality illumination.²⁰ Moreover, commercial warm and neutral WLEDs were used for comparison. Figure S17 presents their EL spectra, which were obviously narrower than the spectra of our WLEDs; in addition, their CRI were only 63.4, and 79.9 and CCT were 2909 and 6730 K. We also compared photographs of 24 color pens taken under these different light sources. As shown in Figure 4g and S10c, the colors under M-CD-based WLEDs were more realistic and richer than those under commercial ones.

The emission spectra of the WLEDs were measured over working time at a driving current of 20 mA to test the stability. As shown in Figure S18, the EL spectra changed by less than 7% after 10 days of continuous operation. It should be noted that the changes in the cyan and red peaks were almost uniform and weak, which resulted in almost no change in their CIE color coordinates (Figure S19), demonstrating that M-CD-based WLEDs possess extraordinary stability.

CONCLUSIONS

In conclusion, we synthesized CDs exhibiting concentration-dependent tunable

fluorescence from CA and hydroxyl-containing amino compounds. Only the M-CD displayed PL tunable over the full visible region. PL from the M-CD was continuously adjusted from 435 to 678 nm as their concentration was adjusted from 0.1 to 100 mg mL⁻¹. The CIE coordinates of different concentrations of M-CD solutions covered 82.3% of the NTSC standard, demonstrating that M-CD have the potential to provide variablecolor displays and lighting by simply changing their concentration. We systematically evaluated the concentration-dependent PL behavior of CDs and demonstrated that the magnitude of the concentration-dependent PL spectral shift of different types of CDs was determined mostly by E_g narrowing but also by the content of C-O-C/C-O-H groups. Different concentrations of M-CD can be uniformly dispersed in epoxy resins to form solids that emit any desired fluorescence color over the full visible region. To illustrate the great potential of these CDs in LED-based display and lighting applications, monochrome blue, cyan, green, yellow, red, and deep red LEDs were fabricated by coating M-CD/epoxy colloids with different emission colors on 405-nm violet LED chips. These LEDs yielded a color gamut covering 99.4% of the NTSC standard and exhibited similar stability decay curves, retaining 94% of their initial EL intensity after 10 days of continuous operation. Furthermore, cyan- and red-emitting M-CD/epoxy colloids were coated on 405-nm LED chips to fabricate warm and neutral WLEDs with color coordinates of (0.430, 0.405) and (0.332, 0.355), respectively, CCT of 3058.7 and 5475.4 K, respectively, luminous efficiency of 41.2 and 46.8 lm W⁻¹, respectively, and ultra-high CRI of 96.4 and 96.6, respectively. Using two different fluorescent conversion layers derived from one material by varying its concentration

greatly simplifies the preparation of high-CRI WLEDs. Uniform weak changes of the PL properties of the cyan and red layers during operation ensured the stability of the M-CD-based WLEDs. This work opens a new door for the exploration of low-cost, easy-to-prepare CDs with tunable PL peak over the full visible range for use in lighting and displays, photovoltaic devices, and biology.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available from the ACS Publications website at http://pubs.acs.org.

Synthesis heating curve; Yields of CDs; Excitation–emission matrices; Concentration– dependent emission peaks; Chemical structures; TEM images; XPS analysis; *Eg* values; Color gamuts; Stability measurements.

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Notes

The authors declare no competing financial interest.

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